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(54) Title: POLYMERS, THEIR PRECURSORS AND PROCESSES FOR PREPARATION THEREOF

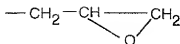
(57) Abstract: Novel block polymers of ethylenically unsaturated monomers and ethylenically unsaturated carboxylates such as vinyl acetate may be made by transition metal mediated, atom transfer polymerisation of an ethylenically unsaturated monomer with an α, ω di-functional polymer precursor having repeating units derived from an ethylenically unsaturated carboxylate, such as vinyl acetate. Also, novel α, ω di-functional polymer precursors may be made by the steps of (a) reacting an ethylenically unsaturated carboxylate with a radical initiator having a substitutable functional group; and (b) substituting the functional groups on the product of step (a) with substituents active for the formation of block polymers in a transition metal mediated, atom transfer polymerisation process.

styrene, acrylates and methacrylates can be prepared by transition metal mediated, atom transfer polymerisation.

- According to a first aspect of the present invention there is provided a process for the preparation of a block polymer which process comprises a transition metal mediated, atom transfer polymerisation of an ethylenically unsaturated monomer with an α, ω -functional polymer precursor having repeating units derived from an ethylenically unsaturated carboxylate. A preferred ethylenically unsaturated carboxylate is vinyl acetate. Such block polymers are believed to be of the ABA type.

- According to this aspect of the present invention, the transition metal mediated, atom transfer polymerisation may be preformed in the presence of (i) a first component represented by MY where M is a transition metal in a low valency state or a transition metal in a low valency state co-ordinated to at least one co-ordinating non-charged ligand and Y is a monovalent or polyvalent counterion, (ii) an organodiimine, (iii) the α, ω di-functional polymer precursor and (iv) an ethylenically unsaturated monomer.

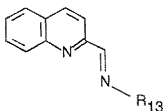
- The ethylenically unsaturated monomer may be : styrene; acrylonitrile; methacrylonitrile; acrylamide; methacrylamide; acrylic acid; unsubstituted acrylate for example having a formula $H_2C=CH-CO_2Z$ in which Z is methyl, allyl, or a functional group such as $-CH_2CH_2OH$ or $-CH_2CH_2N(CH_3)_2$; or a methacrylate for example having a formula $H_2C=C(CH_3)-CO_2Z'$ in which Z' is H, methyl, allyl, benzyl, or a functional group such as $-CH_2CH_2OH$, $-CH_2CH_2N(CH_3)_2$, $-CH_2-CH=CH_2$, $-CH_2NH_3^+Cl^-$ or



- In the first component represented by MY, M is a transition metal in a low valency state or a transition metal in a low valency state co-ordinated to at least one co-ordinating non-charged ligand and Y is a monovalent or polyvalent counterion. Suitable transition metals, M may be Cu(I), Fe(II), Co(II), Ru(II) and Ni(II), preferably, Cu(I). The non-charged ligand may be CH_3CN . Y may be chosen from Cl, Br, F, I, NO_3 , PF_6 , BF_4 , SO_4 , CN, SPh, SCN, SePh or triflate (CF_3SO_3).

- Suitably, the transition metal component and the organodiimine are present as a complex represented by the formula $[ML_m]^{n+} A^{n-}$ wherein M is a transition metal in a low

or a quinoline carbaldehyde such as represented by Formula (4) :



5

Formula (4)

- wherein R_1 , R_2 , R_{10} , R_{11} , R_{12} , and R_{13} may be varied independently and R_1 , R_2 , R_{10} , R_{11} , R_{12} and R_{13} may be H, straight chain, branched chain or cyclic saturated alkyl, hydroxyalkyl, carboxyalkyl, aryl (such as phenyl or substituted phenyl where substitution is as described for R_4 to R_9), CH_2Ar (where Ar = aryl or substituted aryl) or a halogen. Preferably, R_1 , R_2 , R_{10} , R_{11} , R_{12} , and R_{13} may be a C_1 to C_{20} alkyl, hydroxyalkyl or carboxyalkyl in particular C_1 to C_4 alkyl, especially methyl or ethyl, n-propyl, isopropyl, n-butyl, *sec*-butyl, *tert*. butyl, cyclohexyl, 2-ethylhexyl, octyl, decyl or lauryl. R_1 , R_2 , R_{10} , R_{11} , R_{12} , and R_{13} may especially be methyl.

- R_3 to R_9 may independently be selected from the group described for R_1 , R_2 , R_{10} , R_{11} , R_{12} , and R_{13} and OCH_{2n+1} (where n is an integer from 1 to 20), NO_2 , CN , and $O=CR$ (where R = alkyl, benzyl $PHCH_2$ or a substituted benzyl, preferably a C_1 to C_{20} alkyl, especially a C_1 to C_4 alkyl).

- The organodiimine may exhibit a chiral centre α to one of the nitrogen groups. Compounds of Formula (2) may comprise one or more fused rings on the pyridine group.

- One or more adjacent R_1 and R_3 , R_3 and R_4 , R_4 and R_2 , R_{10} and R_9 , R_8 and R_9 , R_3 and R_7 , R_7 and R_6 , R_6 and R_5 groups may be C_5 to C_8 cycloalkyl, cycloalkenyl, polycycloalkyl, polycycloalkenyl or cyclicaryl, such as cyclohexyl, cyclohexenyl or norbornenyl.

- Preferred organodiimines include compounds represented by Formula (2) in which $R_5 = R_6 = R_7 = R_8 = R_9 = H$ and R_{10} is selected from the group consisting of : C_2H_5 -, $n-C_3H_7$ -, $(CH_3)_2CH$ -, $cycloC_3H_5$ -, $n-C_3H_{11}$ -, $n-C_6H_{13}$ -, $n-C_7H_{15}$ -, $n-C_8H_{17}$ -, $n-C_9H_{19}$ -, $n-C_{18}H_{37}$ -, $CH_3(C_2H_5)CH-CH_2$ -, $HO-CH_2-CH_2$ -, $HO-CH_2-CH_2-CH_2$ -,

The transition metal, mediated atom transfer polymerisation process may be preformed using conditions known in the art, for example such as described in International patent publication WO 97/47661, the contents of which are hereby incorporated by reference.

5 The atom transfer polymerisation process may be performed either using a solvent or in bulk, preferably in bulk due to the formation of gels. Non protic solvents may be used. Suitable solvents include hydrocarbons, anisole, ethyl acetate, diphenyl ether, higher alcohols, water and ketones such as acetone. Preferred solvents are xylene and toluene.

10 The atom transfer polymerisation process generally requires elevated temperature and this depends upon the catalyst system and monomers used. In particular, the polymerisation may be performed at a temperature in the range of -40°C to $+180^{\circ}\text{C}$, preferably 0°C to 150°C , more preferably in the range 10° to 130°C . Suitably 90°C may be used, although 110°C may be used for styrene co-polymerisation.

15 The polymerisation process is suitably performed at atmospheric pressure, although a higher pressure might be used.

In the polymerisation process, the molar ratio of ethylenically unsaturated monomer : α, ω di-functional polymer precursor initiator is suitably (3 to 100000) : 1, preferably (10 to 1000) : 1 more preferably (10 to 500) : 1.

20 In the polymerisation process, the molar ratio of organodiimine ligand : transition metal is suitably (100 to 0.1) : 1, preferably (3 to 1) : 1.

In the polymerisation process, the molar ratio of α, ω di-functional polymer precursor initiator : transition metal is suitably (1000 to 0.01) : 1, preferably (10 to 0.5) : 1.

25 In the polymerisation process the concentration of monomer is suitably in the range 1 to 100 %, preferably in the range 20 to 50 %.

The α, ω di-functional polymer precursor acts as an initiator for the transition metal, atom transfer polymerisation process.

30 The α, ω di-functional polymer precursor may be a polymer precursor having a molecular weight in the range from 500 to 50000, preferably from 1000 to 20000 and being represented by the formula :

Preferably, the ethylenically unsaturated carboxylate is vinyl acetate optionally with other co-monomers known in the art.

Preferably, the radical initiator has a functional group selected from hydroxyl, carboxylic acid and amides, preferably hydroxyl. Suitably, the radical initiator having a hydroxyl function group is selected from hydrogen peroxide, azobis compounds having hydroxyl or amide functional groups and benzoyl peroxide. Suitable azobis compounds are:

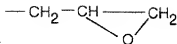
- 4,4'-azobis (4-cyanopentanoic acid),
- 2,2'-azobis{2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]-propionamide},
- 2,2'-azobis{2-methyl-N-[1,1-bis(hydroxymethyl)-ethyl]-propionamide} , and
- 2,2 - azobis(isobutyramide) dihydrate.

The reaction between the ethylenically unsaturated carboxylate with a radical initiator having a substitutable functional group in step (a) may be performed using conventional free radical polymerisation conditions, known in the art.

- In step (b) the functional groups on the product of step (a) are substituted with substituents active for the formation of block polymers in a transition metal mediated, atom transfer polymerisation process. Preferably, such substituents have chlorine or bromine substituents α to an electron withdrawing activating group. Preferably, the electron withdrawing group of the substituent active for the formation of block polymers in a transition metal mediated, atom transfer polymerisation process is selected from nitrile, ester and phenyl.

Preferably, in step (b) the product from step (a) is reacted with $\text{BrC}(\text{CH}_3)_2\text{C}(\text{O})\text{Br}$.

- In step (b) the functional groups on the product of step (a) may be substituted with substituents active for the formation of block polymers in a transition metal mediated, atom transfer polymerisation process under conventional conditions known in the art. Thus a reaction temperature of 0°C or room temperature may be used, depending upon the exotherm. Atmospheric pressure may suitably be used. Dry solvents are used, for example THF, pyridine and toluene. The brominating agent is added in excess. Hydrogen bromide formed in the reaction may be removed, for example by precipitation as $\text{HBr} \cdot \text{NEt}_3$ with triethylamine.



CH₂-CH=CH₂, -CH₂NH₃⁺Cl⁻ or ; substituted methacrylic; acrylonitrile; methacrylonitrile; acylamide; methacrylamide and styrenic polymer repeating units and is preferably at least one methacrylic, styrenic and/or n-butyl methacrylic repeating unit.

- 5 R" may be selected from the group consisting of: CH₃C(O)-, Y"-C(O)-, PhC(O)-, Ph-, PhCH₂-, CH₃-(CH₂-CH₂-CH₂-CH₂)_z-C(O)-, CH₃-(CH₂-CH=CH-CH₂)_z-C(O)- and substituted phenyl; wherein Y" is an n-alkyl group having up to 18 carbon atoms, Ph is phenyl, z' is an integer up to 5000, z" is an integer up to 5000 and the substituted phenyl is substituted with at least one substituent
- 10 selected from the group consisting of NO₂, OMe, CN, NMe₂, OH, Cl, Br, and F. Preferably, R" is CH₃C(O)-.

- The invention will now be described by reference to the following examples and with reference to Figures 1 to 23 in which Figures 1 (a) to (d) are NMR spectra data, Figure 2 is IR spectra data, Figure 3 is GPC data and Figure 4 is DSC data of polymer
- 15 precursor II according to the present invention; Figures 5 (a) to (d) are NMR spectra data, Figure 6 is IR spectra data and Figure 7 is GPC data of polymer precursor III according to the present invention; Figures 8 (a) to (d) are NMR spectra data, Figure 9 is IR spectra data, Figure 10 is GPC data of polymer precursor IV according to the present invention; Figure 11 is GPC data and Figure 12 is DSC data of polymer prepared in
- 20 Example 6 (a) according to the present invention; Figure 13 is GPC data, Figure 14 is DSC data and Figure 15 is NMR spectra data of polymer prepared in Example 6 (b) according to the present invention; Figure 16 is GPC data, Figure 17 is DSC data and Figure 18 is NMR spectra data of polymer prepared in Example 6 (c) according to the present invention; Figure 19 is GPC data and Figure 20 is NMR spectra data of polymer
- 25 prepared in Example 6 (d) according to the present invention; and Figure 21 is GPC data, Figure 22 is DSC data and Figure 23 is NMR spectra data of polymer prepared in Example 6 (e) according to the present invention.

Preparation of Polymer Precursors

Example 1 : Preparation of Polymer Precursor I

- 30 HO(CH₂CH(OAc))_x(CH(OAc)CH₂)_yOH

The polymer precursor was characterised by ^1H NMR, ^{13}C NMR and ^1H - ^{13}C correlation NMR and as well as by COSY, IR and GPC.

Example 3: Preparation of Polymer Precursor II

$\text{Br}(\text{Me})_2\text{CC}(\text{O})\text{O}(\text{CH}_2\text{CH}(\text{OAc}))_2(\text{CH}(\text{OAc})\text{CH}_2)_2\text{OC}(\text{O})\text{CMe}_2\text{Br}$.

5

This illustrates step (b) of the polymer precursor preparation process according to the present invention.

The polymer precursor I prepared in Example 2 (14.08 g, 15.3 mmol) was dissolved in anhydrous tetrahydrofuran (300 mL) with triethylamine (5.20 mL, 37.3 mmol) under nitrogen. 2-Bromoisobutyryl bromide (4.20 mL, 34.0 mmol) was added dropwise with vigorous stirring at 0°C and the reaction mixture stirred at room temperature overnight. The resulting precipitate was filtered off, the tetrahydrofuran removed *in vacuo* and the resulting viscous oil dissolved in dichloromethane. The solution was washed with saturated hydrogen carbonate (3 x 50 mL), dried over anhydrous magnesium sulphate and the dichloromethane removed under high vacuum to give a bright orange oil.

The polymer precursor was characterised by ^1H NMR (Figure 1(a)), ^{13}C pendants NMR (Figure 1(b)), COSY (Figure 1(c)) and ^1H - ^{13}C correlation NMR (Figure 1(d)), IR (Figure 2) and GPC (Figure 3). The compound prepared by the same method, but from a different batch was also characterised by DSC (Figure 4) (sample weight 1.000 mg).

TABLE 2 - Data for Figure 1(b) Example 3 (API 36)

NAME : Nov23-1998		EXPNO : 34	PROCNO : 1
<u>F2 - Acquisition Parameters</u>			
5	Date	981123	Time 20.49
	INSTRUM	dpx300	p2 50000000.00 usec
	PULPROG	pendant	p4 50000000.00 usec
	TD	65536	CNST2 500000.0000000
	SOLVENT	CDCl3	d4 50000000.00000000 sec
10	NS	128	d15 50000000.00000000 sec
	SWH	18832.393 Hz	D1 500000.00000000 sec
	AQ	1.7400308 sec	NUC2 1H
	RG	4096	SF01 75.4763978 MHz
	DE	6.00 usec	NUC1 13C
15	<u>F2 - Processing Parameters</u>		
	SI	32768	LB 2.00 Hz
	WDW	EM	GB 0
<u>1D NMR plot parameters</u>			
20	PPMCM	5.64103 ppm/cm	HZCM 425.71533 Hz/cm

TABLE 4 - Data for Figure 1(d) Example 3 (APJ 36)

	NAME : Nov23-1998		EXPNO : 33	PROCNO : 1
	<u>F2 - Acquisition Parameters</u>			
5	Date	981123	Time	20.30
	INSTRUM	dpx300	p2	50000000.00 sec
	PULPROG	inv4gs	d0	50000000.00000000 sec
	TD	1024	CNST2	500000.00000000
	SOLVENT	CDCl3	d2	50000000.00000000 sec
10	NS	2	d12	50000000.00000000 sec
	SWH	2495.010 Hz	d13	50000000.00000000 sec
	AQ	0.2052596 sec	d20	50000000.00000000 sec
	RG	13004	D1	500000.00000000 sec
	DE	6.00 usec	SF01	300.1307992 MHz
15	NUC1	1H	NUC2	13C
	<u>F1 - Acquisition Parameters</u>			
	NDO	2	FIDRES	130.643814 Hz
	TD	128	SW	221.562 ppm
	SF01	75.47522 MHz		
20	<u>F2 - Processing Parameters</u>			
	SI	2048	LB	0.00 Hz
	WDW	QSINE	GB	0
	<u>F1-Processing Parameters</u>			
	SI	1024	SSB	5
25	MC2	QF	LB	0.00 Hz
	SF	75.4677190 MHz	GB	0
	WDW	QSINE		
	<u>2D NMR plot parameters</u>			
	F2PPMCM	0.26816 ppm/cm	F2HZCM	80.48398 Hz/cm
30	F1PPMCM	11.07808 ppm/cm	F1HZCM	836.03729 Hz/cm

Example 4 : Preparation of Polymer Precursor III

$\text{HOCH}_2\text{CH}_2\text{NHC(O)-C(Me)}_2(\text{CH}_2\text{CH(OAc)})_4(\text{CH(OAc)CH}_3)_2\text{C(Me)}_2\text{C(O)-NH-CH}_2\text{-CH}_2\text{-OH}$

This illustrates step (a) of the polymer precursor preparation process according
 5 to the present invention.

Vinyl acetate and 1-propanol were deoxygenated by a stream of nitrogen for at
 least 30 minutes immediately prior to use. To a mixture of deoxygenated vinyl acetate
 (107.7 mL) and 1-propanol (200 mL) was added to the Azo initiator (Wako, VA-086)
 (2.8835g) having the formula :

10 $\text{HOCH}_2\text{CH}_2\text{NH C(O)C(Me)}_2\text{N=NC(Me)}_2\text{C(O)NH-CH}_2\text{CH}_2\text{OH.}$

The solution was refluxed under a nitrogen atmosphere overnight at 104°C. The
 initiator dissolved on warming. A biphasic solution was obtained on cooling the reaction
 mixture. The solvent was removed *in vacuo* and any remaining water removed by an
 azeotropic distillation using toluene.

15 From GPC, $M_n = 8930$ (using methyl methacrylate standards). Yield was 85 %.

The polymer precursor was characterised by ^1H NMR (Figure 5(a)), ^{13}C pendant
 NMR (Figure 5(b)), COSY (Figure 5(c)) and ^1H - ^{13}C correlation NMR (Figure 5(d))
 as well as by IR (Figure 6) and GPC (Figure 7).

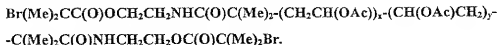
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TABLE 7 - Data for Figure 5(b) Example 4 (APJ 14)

	NAME : Feb08-1999		EXPNO : 22	PROCNO : 1
	<u>F2 - Acquisition Parameters</u>			
5	Date	990208	Time	23.25
	INSTRUM	dpx300	p2	50000000.00 usec
	PULPROG	pendant	p4	50000000.00 usec
	TD	65536	CNST2	500000.0000000
	SOLVENT	CDCl3	d4	50000000.00000000 sec
10	NS	512	d15	50000000.00000000 sec
	SWH	18832.393 Hz	D1	500000.00000000 sec
	AQ	1.7400308 sec	NUC2	1H
	RG	11585.2	SF01	75.4763978 MHz
	DE	6.00 usec	NUC1	13C
15	<u>F2 - Processing Parameters</u>			
	SI	32768	LB	2.00 Hz
	WDW	EM	GB	0
	<u>1D NMR plot parameters</u>			
20	PPMCM	5.64103 ppm/cm	HZCM	425.71533 Hz/cm

TABLE 9 - Data for Figure 5(d) Example 4 (APJ 14)

	NAME : Feb08-1999		EXPNO : 24	PROCNO : 1
	<u>F2 - Acquisition Parameters</u>			
5	Date	990208	Time	23.28
	INSTRUM	dpx300	p2	50000000.00 sec
	PULPROG	inv4gs	d0	50000000.00000000 sec
	TD	1024	CNST2	500000.00000000
	SOLVENT	CDCI3	d2	50000000.00000000 sec
10	NS	2	d12	50000000.00000000 sec
	SWH	2637.131 Hz	d13	50000000.00000000 sec
	AQ	0.1942004 sec	d20	50000000.00000000 sec
	RG	13004	D1	500000.00000000 sec
	DE	6.00 usec	SF01	300.1310966 MHz
15	NUC1	1H	NUC2	13C
	<u>F1 - Acquisition Parameters</u>			
	NDO	2	FIDRES	130.643814 Hz
	TD	128	SW	221.562 ppm
	SF01	75.47522 MHz		
20	<u>F2 - Processing Parameters</u>			
	SI	2048	LB	0.00 Hz
	WDW	QSINE	GB	0
	<u>F1-Processing Parameters</u>			
	SI	1024	SSB	5
25	MC2	QF	LB	0.00 Hz
	SF	75.4677190 MHz	GB	0
	WDW	QSINE		
	<u>2D NMR plot parameters</u>			
	F2PPMCM	0.28344 ppm/cm	F2HZCM	85.06844 Hz/cm
30	F1PPMCM	11.07808 ppm/cm	F1HZCM	836.03729 Hz/cm

Example 5 : Preparation of Polymer Precursor IV

- 5 This illustrates step (b) of the polymer precursor preparation process according to the present invention. The polymer precursor III prepared in Example 4 (38.93 g, 4.36 mmol) was dissolved in anhydrous tetrahydrofuran (300 mL) with triethylamine (1.46 mL, 10.46 mmol) under nitrogen. 2-Bromoisobutyryl bromide (1.29 mL, 10.5 mmol) was added dropwise with vigorous stirring at 0°C and the reaction mixture stirred
- 10 at room temperature overnight. The resulting precipitate was filtered off, the tetrahydrofuran removed *in vacuo* and the resulting viscous oil dissolved in dichloromethane. The solution was washed with saturated hydrogen carbonate (3 x 50 mL), dried over anhydrous magnesium sulphate and the dichloromethane removed under high vacuum to give a bright orange oil.
- 15 The polymer precursor was characterised by ¹H NMR (Figure 8(a)), ¹³C pendant NMR (Figure 8(b)), COSY (Figure 8(c)) and ¹H- ¹³C correlation NMR (Figure 8(d)) as well as by IR (Figure 9) and GPC (Figure 10).

TABLE 12 - Data for Figure 8(b) Example 5 (APJ 58)

	NAME : Mar17-1999	EXPNO : 12	PROCNO : 1
	<u>F2 - Acquisition Parameters</u>		
5	Date	990317	Time 23.42
	INSTRUM	dpx300	p2 50000000.00 usec
	PULPROG	pendant	p4 50000000.00 usec
	TD	65536	CNST2 500000.0000000
	SOLVENT	CDCl3	d4 50000000.00000000 sec
10	NS	512	d15 50000000.00000000 sec
	SWH	18832.393 Hz	D1 500000.00000000 sec
	AQ	1.7400308 sec	NUC2 1H
	RG	7298.2	SF01 75.4763978 MHz
	DE	6.00 usec	NUC1 13C
15	<u>F2 - Processing Parameters</u>		
	SI	32768	LB 2.00 Hz
	WDW	EM	GB 0
	<u>1D NMR plot parameters</u>		
20	PPMCM	5.64103 ppm/cm	HZCM 425.71533 Hz/cm

TABLE 14 - Data for Figure 8(d) Example 5 (APJ 58)

	NAME : Mar17-1999		EXPNO : 14	PROCNO : 1
	<u>F2 - Acquisition Parameters</u>			
5	Date	990317	Time	23.46
	INSTRUM	dpx300	p2	50000000.00 sec
	PULPROG	inv4gs	d0	50000000.00000000 sec
	TD	1024	CNST2	500000.00000000
	SOLVENT	CDCl3	d2	50000000.00000000 sec
10	NS	2	d12	50000000.00000000 sec
	SWH	2653.928 Hz	d13	50000000.00000000 sec
	AQ	0.1929716 sec	d20	50000000.00000000 sec
	RG	6502	D1	500000.00000000 sec
	DE	6.00 usec	SF01	300.1310520 MHz
15	NUC1	1H	NUC2	13C
	<u>F1 - Acquisition Parameters</u>			
	NDO	2	FIDRES	130.643814 Hz
	TD	128	SW	221.562 ppm
	SF01	75.47522 MHz		
20	<u>F2 - Processing Parameters</u>			
	SI	2048	LB	0.00 Hz
	WDW	QSINE	GB	0
	<u>F1-Processing Parameters</u>			
	SI	1024	SSB	5
25	MC2	QF	LB	0.00 Hz
	SF	75.4677190 MHz	GB	0
	WDW	QSINE		
	<u>2D NMR plot parameters</u>			
	F2PPMCM	0.28524 ppm/cm	F2HZCM	85.61028 Hz/cm
30	F1PPMCM	11.07808 ppm/cm	F1HZCM	836.03729 Hz/cm

sulphate was removed by filtration, and volatiles were removed under reduced pressure to give the product in quantitative yield as a pale yellow oil.

- ¹H NMR (CDCl₃, 373 K, 400.13 MHz): δ = 8.51 (d, *J* = 3.5 Hz, 1H), 8.26 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.16 (t, *J* = 4.6 Hz, 1H), 3.52 (t, *J* = 7.6 Hz, 2H), 1.63 (sext, *J* = 7.3 Hz, 2H), 0.84 (t, *J* = 7.5 Hz, 3H). ¹³C (CDCl₃, 373K, 100.61 MHz) : δ = 161.51, 154.44, 149.18, 136.28, 124.37, 120.97, 63.08, 23.65, 11.65 ppm. IR (NaCl, film), 3053-2830, 1648, 1587, 1566, 772, 742 cm⁻¹. Bp = 218°C.

Preparation of N-octyl-pyridinal methanimine.

- To a solution of pyridine-2-carboxaldehyde (19 mL, 0.20 mol) and diethyl ether (150 mL) in a 250 mL round-bottomed flask was added octylamine (33.9 mL, 0.20 mol). The reaction mixture was stirred for 1 hour prior to addition of anhydrous magnesium sulphate (25.2 g) and stirring for a further 2 hours. The magnesium sulphate was removed by filtration and was washed with diethyl ether. The ether was subsequently removed by rotary evaporation to give a dark yellow viscous liquid. The liquid was fractionally distilled at 96 °C at 0.04 torr to give a pale yellow liquid. Yield = 40.5 g (90.5%). ¹H NMR (CDCl₃, 298 K, 250.13 MHz) δ = 8.60 (d, *J* = 4.9 Hz, 1H), 8.33 (s, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 6.2 Hz, 1H), 3.63 (t, *J* = 7.0 Hz, 2H), 1.68 (m, *J* = 7.0 Hz, 2H), 1.26 (m, *J* = 7.3 Hz, 10H), 0.82 (t, *J* = 7.0 Hz, 3H). ¹³C (CDCl₃, 298K, 100.16 MHz) : 161.1, 154.5, 148.8, 135.7, 123.9, 120.5, 61.1, 31.5, 30.4, 29.1, 28.9, 27.0, 22.3, 13.7. Anal. Calc. for C₁₄H₂₂N₂ : C = 77.01, H = 10.16, N = 12.82. Found C = 77.15, H = 10.25, N = 12.85.

General procedure for atom transfer polymerisation.

- Monomers were passed down a basic alumina column (Aldrich, Brockmann I grade) immediately prior to use, degassed by a stream of nitrogen for at least 30 minutes and freeze-pump-thawed (three times). Solvents were deoxygenated by a stream of nitrogen for at least 30 minutes prior to use. Cu(I)Br was purified according to a published procedure (Keller, R.N. and Weycoff, M.D. Inorg. Synth. 1947, 2,1.). All atom transfer polymerisation experiments carried out at 90°C except for those involving styrene which were heated to 110°C. A slight excess of ligand (10%) is added to the reaction mixture.

The atom transfer polymerisation experiments have been carried out using slightly varying methods.

TABLE 16 - GPC ANALYSIS Figure 11 Example 6(a)

	Sample name : aj1789		Raw data filename : 02112.017	
	<u>Conditions :</u>			
5	Solvent :	THF with toluene	Temperature :	room temp.
	Column set :	one guard column and 2 mixed D	Flow rate :	1.00 mL/min
	Detector :	DRI/UV		
	<u>Data Processing :</u>			
	Method :	2	Calibration using :	Narrow standards
10	Calibration limits :	10.00 to 20.65 Mins		
	Curve used :	3 rd order polynomial	Coefficients :	Log(M) = A + BT + CT ² + DT ³
		A=11.819727, B = 0.759678, C = 0.016374, D = 0.000144		
	Last calibrated :	Wed Oct 21 10:54:26 1998		
	Flow rate marker :	found at 20.67 in standards at 20.38 Mins.		
15	Broad peak start :	11.08	end :	15.08 Mins.
		Standards		Sample
	K :	10.4000*10e-5		10.4000* 10e-5
	alpha :	0.697		0.697
	<u>Molecular weight results :</u>			
20	Mp = 35898	Mn = 27342	Mw = 41579	
	Mz = 58673	Mz+1 = 76178	Mv = 39238	
	Polydispersity = 1.521	Peak area = 5112		

- The polymer precursor was also characterised by DSC (Figure 12) (3.000 mg sample weight Total Mn - 33000 heat from -50.00°C to 140.00°C at 20.00°C/min).

This example (Example 6(a)) was repeated using different monomers and different molar ratios of reagents as follows :

Example 6 (b) : The monomer used was methyl methacrylate.

Molar ratio of monomer : polymer precursor : metal : ligand = 50 : 1 : 2 : 4.

- Product Mn = 14490 using poly(methyl methacrylate) standard for GPC (Figure 13).

TABLE 18 - GPC ANALYSIS Figure 16 Example 6(c)

Sample name : apj1669		Raw date filename : 29102.009
<u>Conditions :</u>		
5	Solvent : THF with toluene	Temperature : room temp.
	Column set : one guard column and 2 mixed D	Flow rate : 1.00 mL/min
	Detector : DRI/UV	
<u>Data Processing :</u>		
	Method : 21	Calibration using : Narrow standards
10	Calibration limits : 9.58 to 20.67 Mins	
	Curve used : 3 rd order polynomial	Coefficients : Log(M) = A + BT + CT ² + DT ³
	A=13.147278, B = 1.020344, C = 0.032583, D = 0.000469	
	Last calibrated : Wed Oct 21 11:04:12 1998	
	Flow rate marker : found at 20.67 in standards at 20.40 Mins.	
15	Broad peak start : 11.52	end : 15.85 Mins.
	Standards	Sample
	K : 10.4000*10e-5	10.4000* 10e-5
	alpha : 0.700	0.700
<u>Molecular weight results :</u>		
20	Mp = 24042	Mn = 16442 Mw = 24927
	Mz = 35106	Mz+1 = 45798 Mv = 23556
	Polydispersity = 1.516	Peak area = 7693

The polymer precursor was also characterised by DSC (Figure 17) (1.00 mg sample weight, total Mn - 17000, heat from -50.00°C to 140.00°C at 20.00°C/min) and by ¹H NMR CDCl₃ (Figure 18).

Example 6 (d) : The monomer used was n-butyl methacrylate.

Molar ratio of monomer : polymer precursor : metal : ligand = 100 : 1 : 2 : 4.

Product Mn = 13190 using poly(methyl methacrylate) standard for GPC (Figure 19).

TABLE 20 - GPC ANALYSIS Figure 21 Example 6(e)

Sample name : apj188 30		Raw date filename : 01122.048
<u>Conditions :</u>		
5	Solvent : THF with toluene	Temperature : room temp.
	Column set : one guard column and 2 mixed D	Flow rate : 1.00 mL/min
	Detector : DRI/UV	
<u>Data Processing :</u>		
	Method : 2	Calibration using : Narrow standards
10	Calibration limits : 9.88 to 20.42 Mins	
	Curve used : 3 rd order polynomial	Coefficients : $\text{Log}(M) = A + BT + CT^2 + DT^3$
	A=11.821880, B = 0.759705, C = 0.016359, D = 0.000144	
	Last calibrated : Sun Nov 15 11:08:30 1998	
	Flow rate marker : found at 20.42 in standards at 20.38 Mins.	
15	Broad peak start : 11.83 end : 16.55 Mins.	
	Standards	Sample
	K : 10.4000*10e-5	10.4000* 10e-5
	alpha : 0.697	0.697
<u>Molecular weight results :</u>		
20	Mp = 12694	Mn = 8486 Mw = 13647
	Mz = 20030	Mz+1 = 27335 Mv = 12805
	Polydispersity = 1.608	Peak area = 6699

The polymer precursor was also characterised by DSC (Figure 22) (sample weight 3.200 mg, heat from -50.00°C to 120.00°C at 20.00°C/min) and by ¹H NMR in CDCl₃ (Figure 23).

Example 7: Polymerisation of styrene with polymer precursor IV.

Polymer precursor IV prepared in Example 5 (1.1044 g, 0.4 mmol), Cu(I)Br (0.1139 g, 0.8 mmol) and a magnetic follower were placed in a Schlenk tube. Deoxygenated toluene(4.40 mL) and N-propyl-2-pyridinal methanimine (0.26 g, 1.76 mmol) prepared as hereinbeforedescribed were added and the solution heated to 110°C.

Claims :

1. A process for the preparation of a block polymer which process comprises a transition metal mediated, atom transfer polymerisation of an ethylenically unsaturated monomer with an α, ω di-functional polymer precursor having repeating units derived from an ethylenically unsaturated carboxylate.
2. A process as claimed in claim 1 wherein the ethylenically unsaturated carboxylate is vinyl acetate.
3. A process as claimed in claim 1 wherein the ethylenically unsaturated monomer is selected from the group consisting of styrene, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, acrylic acid, unsubstituted acrylate and methacrylate.
4. A process as claimed in claim 2 wherein the ethylenically unsaturated monomer is selected from the group consisting of styrene, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, acrylic acid, unsubstituted acrylate and methacrylate.
5. An α, ω di-functional polymer precursor having a molecular weight in the range from 500 to 50000 and being represented by the formula :

$$\text{X}[-\text{CH}_2-\text{CY}(\text{OR})-]_x[-\text{CY}'(\text{OR})-\text{CH}_2-]_y-\text{X}'$$
 wherein x and y are integers independently greater than 1; Y and Y' are independently H or $-\text{CH}_3$; R represents a hydrocarbyl group, and X and X' independently represent substituents active for the formation of block polymers in a transition metal mediated, atom transfer polymerisation process.
6. A polymer precursor as claimed in claim 5 wherein R is selected from the group consisting of $\text{CH}_3\text{C}(\text{O})-$, $\text{Y}''-\text{C}(\text{O})-$, $\text{PhC}(\text{O})-$, $\text{Ph}-$, PhCH_2- ,

wherein x and y are integers independently greater than 1; Y and Y' are independently H or $-\text{CH}_3$ and R'' represents a hydrocarbyl group and $-\text{B}-$ represents at least one polymer repeating unit selected from the group consisting of acrylic, substituted acrylic, methacrylic, substituted methacrylic, acrylonitrile, methacrylonitrile, acylamide,

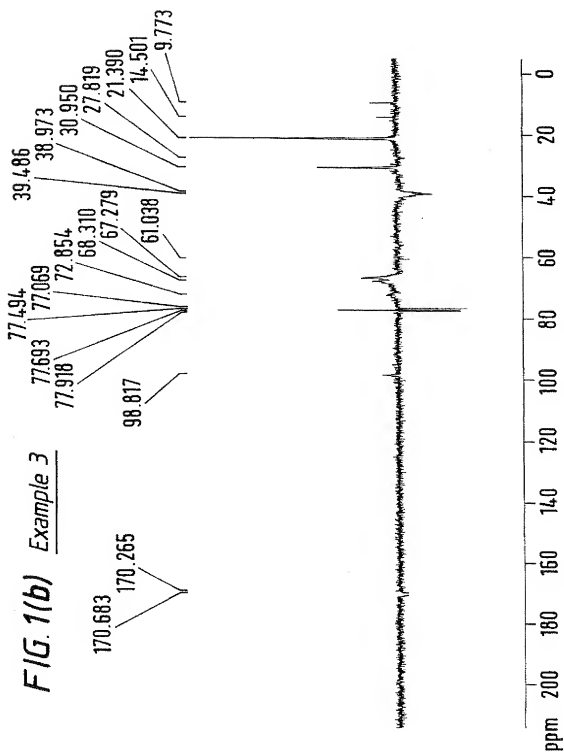
5 methacrylamide and styrenic polymer units.

14. A block polymer as claimed in claim 13 wherein R'' is selected from the group consisting of $\text{CH}_3\text{C}(\text{O})-$, $\text{Y}''-\text{C}(\text{O})-$, $\text{PhC}(\text{O})-$, $\text{Ph}-$, PhCH_2- , $\text{CH}_3-(\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2)_x\text{C}(\text{O})-$, $\text{CH}_3-(\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)_z\text{C}(\text{O})-$ and substituted phenyl, wherein Y'' is an n -alkyl group having up to 18 carbon atoms, Ph is phenyl, z' is

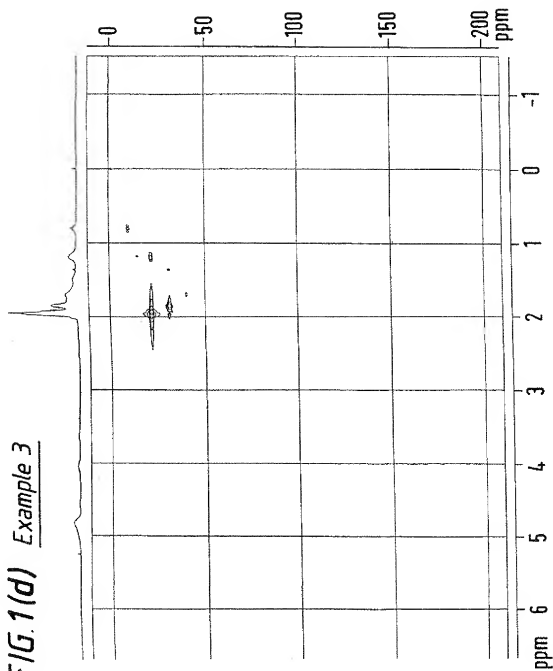
10 an integer up to 5000, z'' is an integer up to 5000 and the substituted phenyl is substituted with at least one substituent selected from the group consisting of NO_2 , OMe , CN , NMe_2 , OH , Cl , Br , and F .

15. A polymer precursor as claimed in claim 13 wherein R'' is $\text{CH}_3\text{C}(\text{O})-$.

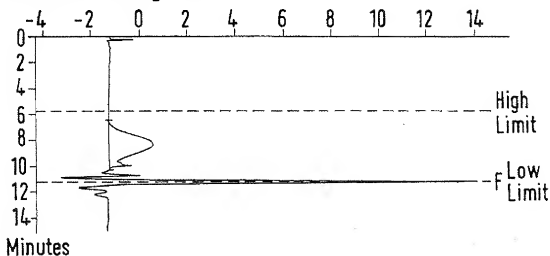
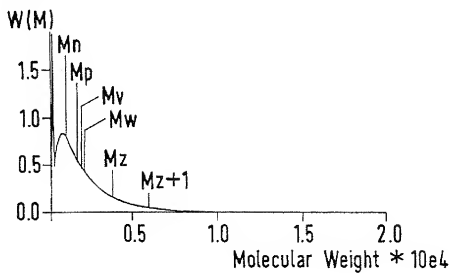
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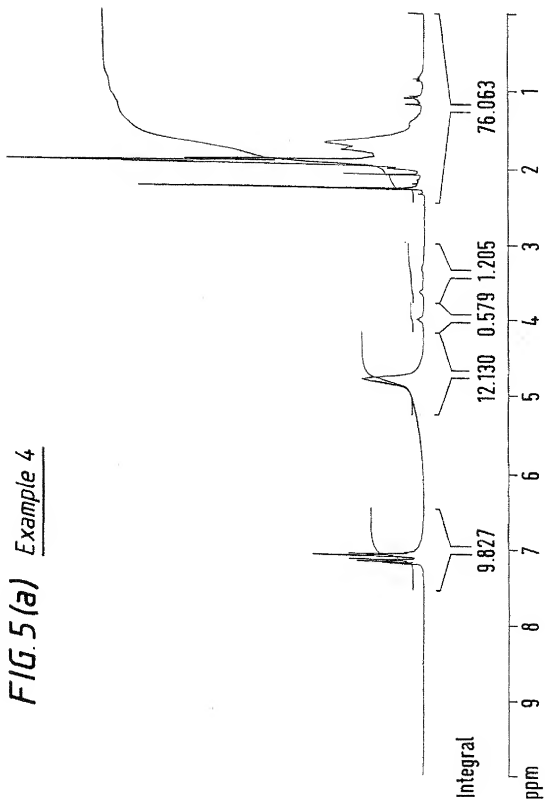
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FIG. 1(d) Example 3

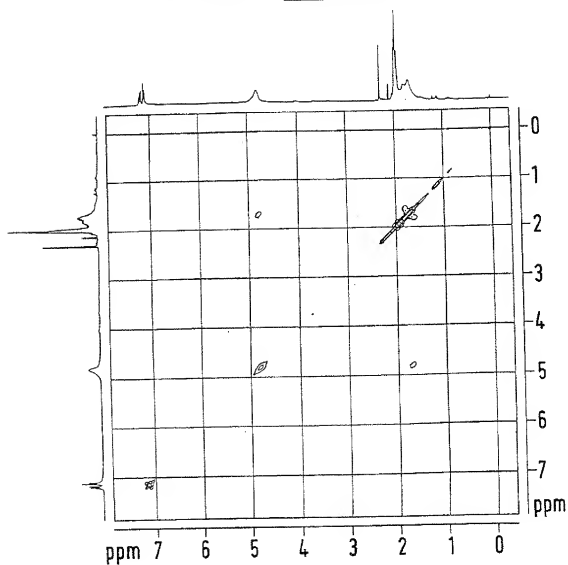
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FIG.3 Example 3*Raw Chromatogram:**W(M) plot:*

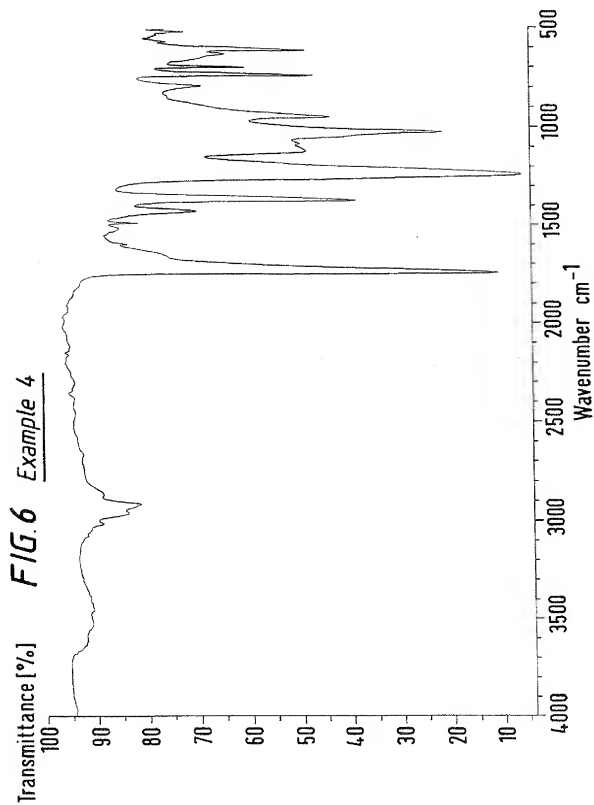
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FIG. 5(a) Example 4

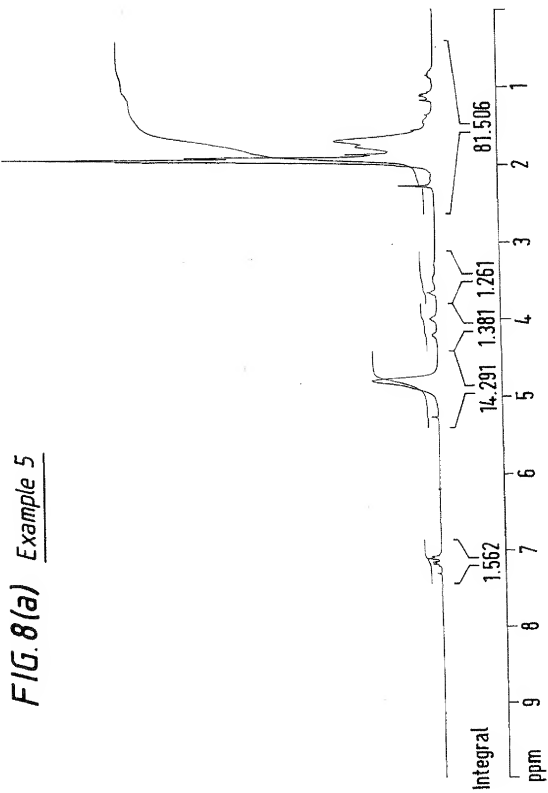
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FIG. 5(c) Example 4

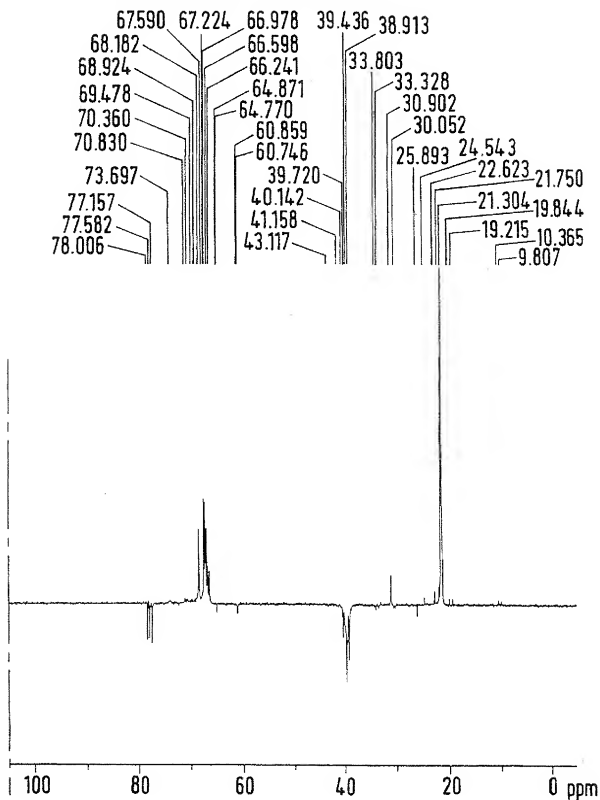
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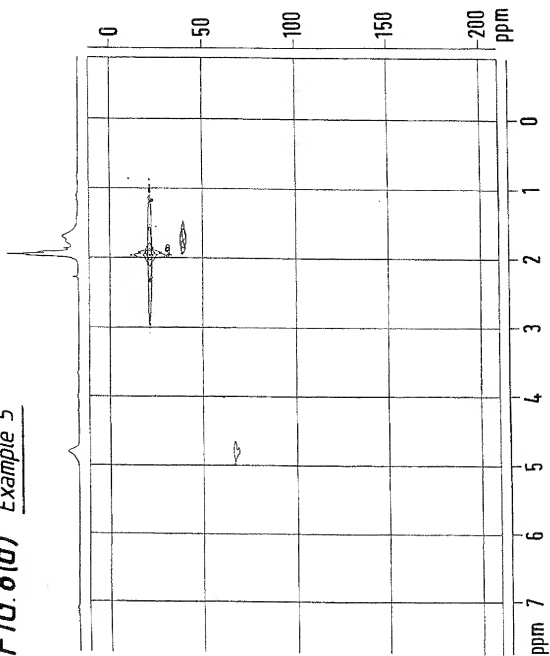
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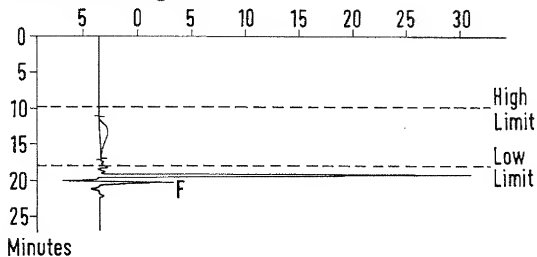
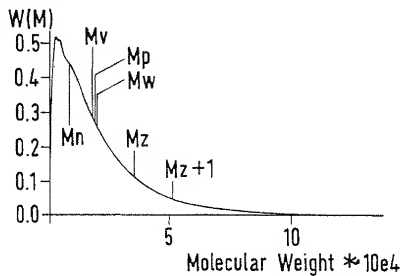
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FIG. 8(b'') Example 5

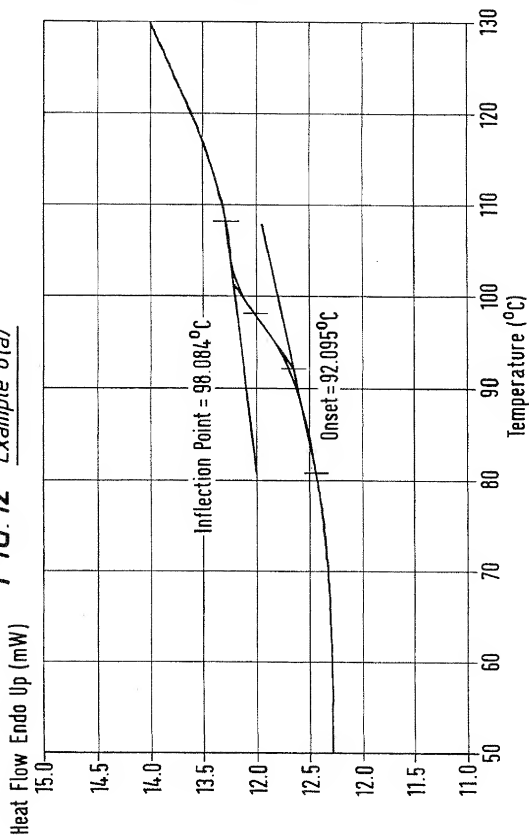
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FIG. 8(d) Example 5

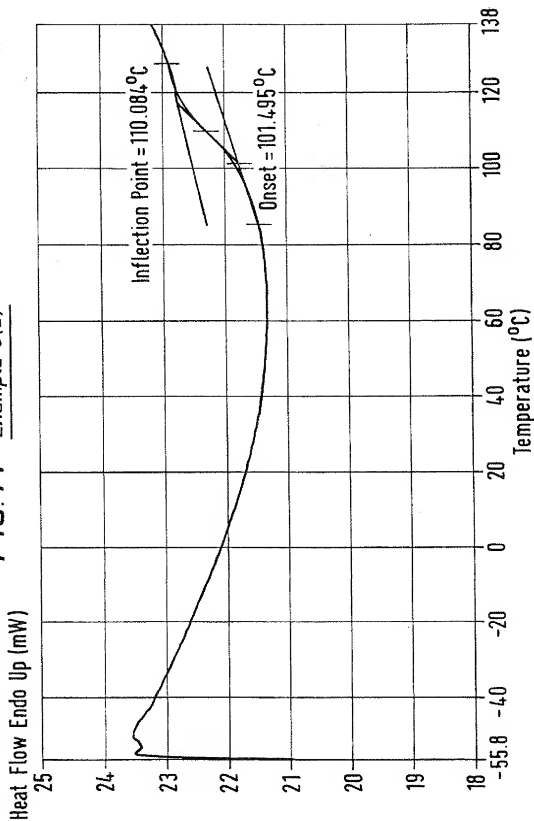
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FIG. 10 Example 5*Raw Chromatogram:**W(M) plot:*

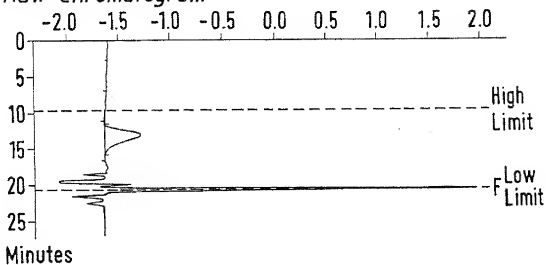
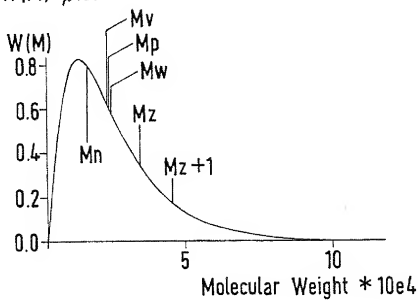
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FIG. 12 Example 6(a)

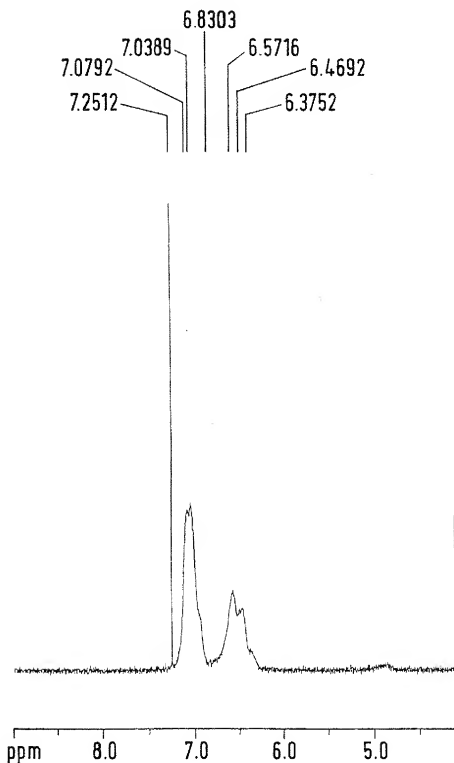
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FIG. 14 *Example 6(b)*

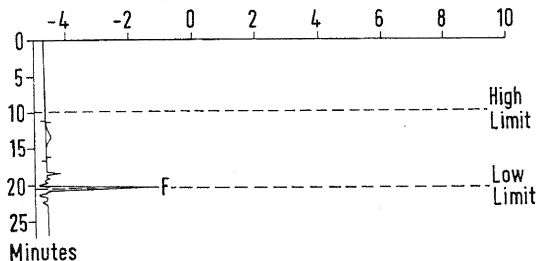
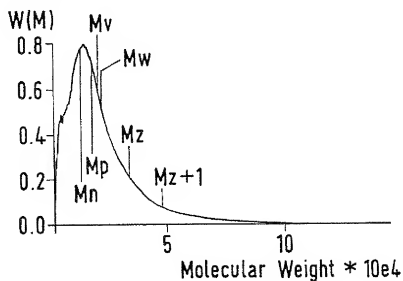
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FIG.16 Example 6(c)*Raw Chromatogram:**W(M) plot:*

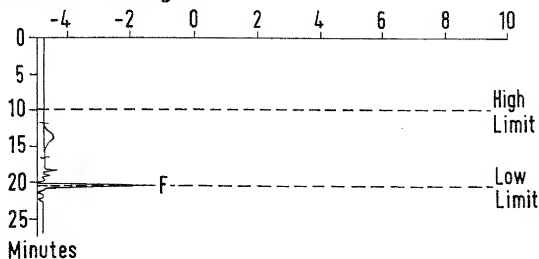
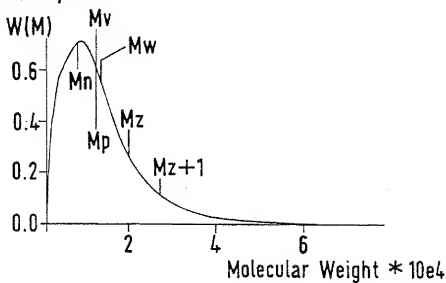
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FIG. 18' Example 6(c)

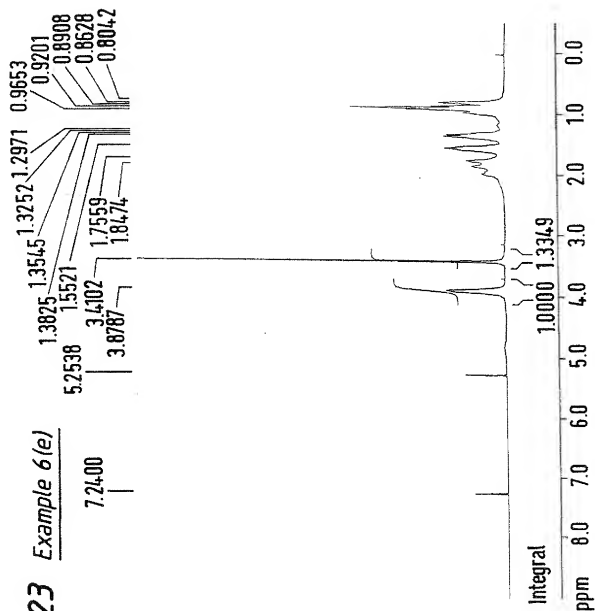
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FIG. 19 Example 6(d)*Raw Chromatogram:**W(M) plot:*

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FIG. 21 Example 6(e)*Raw Chromatogram:**W(M) plot:*

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FIG. 23 *Example 6(e)*

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 00/02120

A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 239 250 A (BASF CORP) 26 June 1991 (1991-06-26) page 4, line 4-16 ---	1,5
A	US 5 789 487 A (MATYJASZEWSKI KRZYSZTOF ET AL) 4 August 1998 (1998-08-04) claim 3 ---	1
P,X	WO 00 11055 A (ATOCHEM ELF SA ;KAPPLER PATRICK (FR); PASCAL THIERRY (FR); BOUTEVI) 2 March 2000 (2000-03-02) page 13, line 9-19 -----	1-4

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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(54) Title: HAIRSPRAY COMPOSITIONS CONTAINING SILICONE BLOCK COPOLYMERS			
(57) Abstract			
<p>The present invention relates to hairspray compositions comprising from about 50 % to about 99.9 % by weight of an alcohol solvent, and from about 0.1 % to about 30 % by weight of a silicone-containing adhesive block copolymer having a weight average molecular weight from about 10,000 grams/mole to about 10,000,000 grams/mole and which is formed from the free radical polymerization of an ethylenically unsaturated monomer with select silicone macroinitiators, preferably silicone macroazoinitiators. The hairspray compositions, when dried, preferably have a cohesive strength of greater than about 0.5 kgf/mm², a total energy absorption per unit volume of greater than about 0.55 kgfmm³, an impact strength of greater than about 7000 ergs, and an improved removability from hair as defined by a hair stiffness value of from 0 to about 3.5 (0 to 4 scale) and a hair flaking value of from 0 to about 3.5 (0 to 4 scale). These hairspray compositions provide improved hair styling performance, and in particular provide improved maintenance or hold when applied to dry hair and causes minimal or no drooping of the hair during or immediately after application.</p>			

HAIRSPRAY COMPOSITIONS CONTAINING SILICONE BLOCK COPOLYMERS

TECHNICAL FIELD

The present invention relates to hairspray compositions which provide improved hair style retention characteristics and hair feel. These compositions comprise a silicone-containing adhesive block polymer and at least about 50% by weight of an alcohol solvent.

BACKGROUND OF THE INVENTION

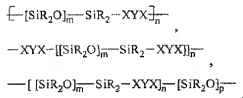
Hair styling compositions are well known and include compositions formulated for and intended for application as shampoos, hairsprays, aerosol mousses, and other formulations known for use in delivering hair styling polymers to the hair. These compositions are typically applied to wet or dry hair, depending on the formulation, and allowed to form thin hair styling films or welds to the applied surface.

Hair styling compositions are commonly formulated as hairsprays intended for application to dry, positioned or styled hair to maintain or hold the position of such dry, styled hair. These hairsprays are typically applied to the hair as pump sprays or from pressurized aerosol canisters. Such compositions provide temporary setting benefits to dry, styled hair and can usually be removed by water or by the next shampooing. The hair styling materials used in hairspray compositions are generally in the form of resins, gums, and adhesive polymers.

Many hairsprays, however, tend to deposit hair styling material on the hair that leaves the hair either excessively stiff or excessively sticky after the material has been applied to the hair and allowed to dry. Excessively stiff hairsprays are brittle and break down under common stresses such as wind, brushing, combing, and often feel or look unnatural. On the other extreme, excessively sticky hairsprays are more flexible under stress and are not excessively brittle, but leave the hair with a heavy, coated feel and a limp appearance as the hair droops and does not readily maintain or hold the intended style of the hair. These excessively sticky hairsprays also cause the hair to quickly become soiled from dust, dirt, lint, sebum, and other common contaminants that more readily adhere to the sticky hairsprays.

Some hairsprays have been formulated which can be applied to clean, dry hair to maintain or hold the desired hair style, and which are neither excessively stiff

weight average molecular weight of from about 10,000 grams/mole to about 10,000,000 grams/mole and which is formed from the free radical polymerization of an ethylenically unsaturated monomer with a silicone macroinitiator, wherein the silicone macroinitiator contains a chemical group selected from the group consisting of



and combinations thereof, wherein each R is independently selected from the group consisting of C1-C10 alkyl, phenyl, C1-C10 alkyl-substituted phenyl, and mixtures thereof; X is a divalent radical; Y is selected from the group consisting of



and combinations thereof; m, n, and p are positive integers each independently having a value of 1 or greater.; and wherein the silicone macroinitiator has a number average molecular weight from about 500 grams/mole to about 500,000 grams/mole, and wherein the hairspray composition, when dried, preferably has a cohesive strength of greater than about 0.5 kgf/mm², a total energy absorption per unit volume of greater than about 0.55 kgfmm/mm³, and an impact strength of greater than about 7000 ergs. The hair spray compositions preferably have improved removeability, wherein improved removeability is defined by a hair stiffness value of from 0 to about 3.5 and a hair flaking value of from 0 to 3.5 (0 to 4 scale)

It has been found that these hairspray compositions are especially effective in providing hair styling performance when applied to dry, styled or positioned hair. In particular, these hairspray compositions can be applied to dry, styled or positioned hair without causing the hair to be excessively stiff or sticky after the hairspray has dried onto the hair, and without causing the dry, styled or positioned hair to excessively droop immediately after application of the hairspray composition and before the applied composition solidifies and sets onto the hair.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates an overhead view of a dumbbell-shaped planar dried hairspray film sample useful for measuring the physical properties such as the cohesive strength and total energy absorption per unit volume as described herein.

to about 99.9%, preferably from about 50% to about 90%, more preferably from about 55% to about 80%, by weight of the hairspray compositions.

Alcohol solvents suitable for use in the hairspray compositions of the present invention are preferably ethanol, n-propanol, isopropanol, and combinations, wherein the selected silicone-containing adhesive block polymer is soluble in the selected alcohol solvent at a concentration of at least about 0.1 mg/mL, preferably at least about 0.5 mg/mL, and more preferably at least about 1 mg/mL, at about 22.7°C.

The hairspray composition may further comprise other additional solvents, including water, provided that the silicone-containing block copolymer remains dissolved or otherwise dispersed in the hairspray composition, and provided that such additional solvents are chemically and physically compatible with the ingredients of the composition and that it does not substantially and unduly impair product performance. The hairspray compositions may further comprise up to about 45% by weight of water, preferably less than about 40%.

It has been found that the alcohol solvent, at the above-described concentrations, when used in combination with the select silicone-containing adhesive block polymers is especially effective at providing improved hair styling performance to the hairspray composition of the present invention. This combination of select polymers and alcohol solvents is even more effective in minimizing or eliminating the undesirable drooping of dry, styled or positioned hair immediately after application to the hair.

Adhesive Block Copolymer

The hairspray composition of the present invention comprises select silicone-containing adhesive block copolymers as defined herein, which help provide the improved hair styling performance to the composition, and which are soluble or dispersible in the alcohol solvent of the hairspray composition. Concentrations of the block copolymers in the hairspray composition ranges from about 0.1% to about 30%, preferably from about 0.5% to about 20%, and more preferably from about 0.5% to about 10%, by weight of the composition.

The silicone-containing adhesive block copolymers selected for use in the hairspray compositions of the present invention are prepared by the free radical polymerization of select silicone containing macroinitiators (described in detail hereinafter) and ethylenically unsaturated monomers. The resulting block copolymers comprise sequentially arranged moieties or blocks which are further composed of smaller repeating units. The silicone-containing adhesive block

be used. The polymerization is allowed to proceed as long as needed for a high level of conversion to be achieved, typically from a few hours to a few days. The solvent is then removed, usually by evaporation or by precipitating the copolymer by addition of a nonsolvent. The resulting block copolymer can be further purified, as desired, and used in formulating the hairspray composition of the present invention by formulation techniques well known in the art.

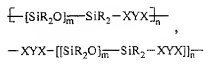
The silicone-containing adhesive block copolymers for use herein can also be made by a semi-continuous or continuous process. In the semi-continuous process, two or more additions of monomers or macromonomers are made during the polymerization reaction. This is advantageous when the copolymer is made of several monomers which react during the polymerization at different rates. The proportions of monomers added to the reaction at the separate points of addition can be adjusted by one of ordinary skill in the art such that the polymers of the final product have a more uniform structure. In other words, the polymers of the final product will have a more consistent monomer content distribution for each of the monomer types charged to the reaction.

Other examples of silicone-containing block copolymers and methods of making them are described in U.S. Patent 5,523,365, to Geck et al., issued June 4, 1996; U.S. Patent 4,689,289, to Crivello, issued August 25, 1987; U.S. Patent 4,584,356, to Crivello, issued April 22, 1986; *Macromolecular Design, Concept & Practice*, Ed: M.K. Mishra, Polymer Frontiers International, Inc., Hopewell Jct., NY (1994); and *Block Copolymers*, A. Noshay and J.E. McGrath, Academic Press, NY (1977), which descriptions are incorporated herein by reference.

Silicone-containing Macroinitiator

The silicone-containing adhesive block copolymers of the hairspray composition herein comprise from about 2% to about 50%, preferably from about 5% to about 40%, and more preferably from about 10% to about 30%, by weight of silicone-containing blocks, wherein the silicone-containing blocks are derived from the select silicone-containing macroinitiators described herein.

The silicone-containing macroinitiator for use in the hairspray composition of the present invention is selected from the group consisting of the following formulas:



about 9. Most preferred are those macroazoinitiators represented by the above formula wherein x is an integer having a value of either about 135 or 67, and n is an integer having a value of from about 6 to about 9.

The silicone-containing blocks (Block A) of the block copolymers herein preferably contain at least about 10 repeating monomer units, more preferably at least about 40 monomer units, even more preferably at least about 60 monomer units, wherein each of the repeating monomer units are derived from the select silicone-containing macroinitiators described herein, and the average molecular weight of each silicone-containing block preferably ranges from about 500 grams/mole to about 60,000 grams/mole, more preferably from about 1,000 grams/mole to about 25,000 grams/mole, even more preferably from about 2,000 grams/mole to about 15,000 grams/mole.

Ethylenically Unsaturated Monomer

The silicone-containing adhesive block copolymers of the hairspray composition herein comprise from about 50% to about 98%, preferably from about 60% to about 95%, and more preferably from about 70% to about 90%, by weight of a copolymerizable ethylenically unsaturated monomers.

The blocks (block B) in the silicone-containing adhesive block copolymer are derived from ethylenically unsaturated monomers, wherein block B has a glass transition temperature (T_g value) of more than about -20°C , more preferably more than about -5°C , and also preferably less than about 60°C , more preferably less than about 50°C , and even more preferably less than about 40°C .

The ethylenically unsaturated monomers are copolymerizable with the silicone-containing macroinitiators and contain at least one polymerizable carbon-carbon double bond, which can be mono-, di-, tri- or tetra-substituted. Preferred are vinyl monomers. Either a single type of ethylenically unsaturated monomer or combination of two or more ethylenically unsaturated monomers can be used. The ethylenically unsaturated monomers are selected to meet the requirements of or preferences for the silicone-containing adhesive block copolymers described herein, including solubility in the selected alcohol solvent, glass transition temperatures within the above-described ranges for hair styling or conditioning performance, reactivity with the selected silicone-containing macroinitiator, and so forth.

The ethylenically unsaturated monomers for use in making the silicone-containing adhesive block copolymers may be hydrophilic or hydrophobic, water soluble or water insoluble. These ethylenically unsaturated monomers are preferably hydrophilic monomers, or combinations of hydrophilic and hydrophobic monomers

methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol(2-methyl-2-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octadecanol, and the like, the alcohols preferably having from about 1 to about 12 carbon atoms; dicyclopentenyl acrylate; 4-biphenyl acrylate; pentachlorophenyl acrylate; 3,5-dimethyladamantyl acrylate; 3,5-dimethyladamentyl methacrylate; 4-methoxycarbonylphenyl methacrylate; trimethylsilyl methacrylate; styrene; alkyl substituted styrenes including alpha-methylstyrene and t-butylstyrene; vinyl esters, including vinyl acetate, vinyl neonanoate, vinyl pivalate and vinyl propionate; vinyl chloride; vinylidene chloride; vinyl toluene; alkyl vinyl ethers, including isobutyl vinyl ether and s-butyl vinyl ether; butadiene; cyclohexadiene; bicycloheptadiene; 2,3-dicarboxymethyl-1,6-hexadiene; ethylene; propylene; indene; norbornylene; β -pinene; α -pinene; salts of acids and amines listed above, and combinations thereof. The quaternized monomers can be quaternized either before or after the free radical copolymerization reaction with the macroinitiator described hereinafter.

Preferred ethylenically unsaturated monomers include acrylic acid, methacrylic acid, N,N-dimethyl acrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, acrylic or methacrylic acid esters of C₁-C₁₈ alcohols, styrene, alpha-methylstyrene, t-butylstyrene, vinyl acetate, vinyl propionate, 2-methoxyethyl acrylate, 2-ethoxyethyl acrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, salts of any acids and amines listed above, and combinations thereof.

Neutralized Block Copolymers

The silicone-containing adhesive block copolymers may comprise acidic functionalities, such as carboxyl groups, and are usually used in at least partially neutralized form to promote solubility or dispensability of the block copolymer in the alcohol solvent defined herein. In addition, use of the neutralized form aids in the ability of the hair styling spray compositions to be removed from the hair by shampooing. The extent of such neutralization ranges from about 10% to 100%, more preferably from about 20% to about 90%, even more preferably from about

t-butyl acrylate: 40%; n-butyl acrylate: 28%; acrylic acid: 12%; methacrylic acid: 10%;

silicone macroazoinitiator (above-described formula, $x=135$, n is from about 6 to about 9) 10%;

Molecular weight of silicone block: 10,000 grams/mole

Polymer molecular weight: 114,000 grams/mole.

[Poly(dimethyl siloxane)-block-poly(t-butyl acrylate-co-acrylic acid)] $_n$

t-butyl acrylate: 40%; n-butyl acrylate: 24%; acrylic acid: 21%;

silicone macroazoinitiator (above-described formula, $x=135$, n is from about 6 to about 9) 15%;

Molecular weight of silicone block: 10,000 grams/mole.

Polymer molecular weight: 86,000 grams/mole.

[Poly(dimethyl siloxane)-block-poly(t-butyl acrylate-co-ethyl acrylate-co-acrylic acid)] $_n$

t-butyl acrylate: 32%; ethyl acrylate: 33%; acrylic acid: 20%;

silicone macroazoinitiator (above-described formula, $x=67$, n is from about 6-9) 15%.

Polymer molecular weight: 110,600 grams/mole.

Molecular weight of silicone block: 5000 grams/mole.

The preferred silicone-containing macroazoinitiators described above are available from Wako Chemical USA, Inc., Richmond, Virginia, USA as VPS1001 and VPS 0501 (poly(dimethylsiloxane) initiators).

Properties of the Dried Hairspray Compositions

The hairspray compositions of the present invention, when dried, preferably have specific physical properties as defined by cohesive strength, total energy absorption per unit area, impact strength and improved removeability (defined in terms of hair stiffness and flaking values). Each of these preferred physical properties is described in detail hereinafter.

Cohesive Strength (kgf/mm²)

Cohesion is the strength of the bonds formed within a sample, e.g., a dried hairspray composition. The cohesive strength, which is designated as kgf/mm² (kilograms of force per square millimeter) is the maximum unit stress a material will

sections between the wide ends and the narrow section of the film are about 6.5 mm. in length (i.e. $(5-3)/2 = 6.5$ mm.). Also the end portions of the narrow, center portion should be smoothly curved to avoid any stress points in the sample. The curve of the transition section, should have a radius, R , of from about 0.5 in. to about 5 inches, and should join tangentially to the narrow section. The film is formed to a thickness, t , of 0.4 mm. ($t = 0.4$ mm.). The dumbbell shaped samples are further equilibrated to a "constant weight". By "constant weight" is meant that over a selected 4 day period, there is no more than 0.2% average weight gain or loss, relative to the dumbbell's measured weight 4 days previous and no more than $\pm 0.2\%$ weight drift should be observed between two consecutive measurements in the four day period of time. The dumbbell should be tested within a 7 day period of reaching this constant weight.

The samples are tested on a calibrated Instron Model Mini-55 tensile tester. Before mounting the sample into the Instron, the length, L , width, b , and thickness, t , of the narrow section of the dumbbell shaped sample are measured to the nearest micron with a calibrated micrometer. The dimensional measurements are required by the Instron for force per unit area calculations. The wide ends of the dumbbell samples are clamped into the Instron and pulled at a crosshead rate of 5 mm. per minute. The Instron tester measures the overall forces (e.g., kgf) applied to the film. These forces are spread over the cross sectional area of the narrow section of the film. The cohesive strength of the copolymer is the maximum unit force measured by the Instron divided by the cross sectional area of the narrow portion of the film.

The dried hairspray compositions of the present invention have a cohesive strength of greater than about 0.5 kgf/mm^2 , preferably greater than about 0.6 kgf/mm^2 , and more preferably greater than about 0.7 kgf/mm^2 .

Total Energy Absorption Per Unit Volume (e.g., kgfmm/mm^3)

The total energy absorption per unit volume, which is designated as kgfmm/mm^3 (kilograms of force millimeters per millimeter cubed), is the ratio of the total energy required to reach the autobreak point (in $\text{kgf} \times \text{mm}$) to the original volume of the sample (mm^3). The total energy required to reach the break point is calculated using standard techniques by determining the area under a load versus displacement curve for the sample. The total energy absorption per unit volume is also known as "toughness" by those skilled in the art of polymer science and materials testing.

The measurements are made at about 22.7°C and about 50% relative humidity.

The dried hairspray compositions of the present invention preferably have a total energy absorption per unit volume of greater than about 0.55 kgfmm/mm^3 ,

Turn on the instrument switch, to drop the probe onto the sample. The first step in the measurement of impact energy is to find the range of probe height necessary to fracture the film. Start at 1 mm for the first step. Continue to move up according to the suggested distance progression until a fracture is observed. When a fracture is observed make a note of it and move to a new sample. The second step in determining impact energy is to set a new sample and start drop at an observed fracture point in the range procedure. Set a new film sample and move the probe to the next lowest setting. If the film fractures, record result and repeat previous step. If the film does not fracture, set a new sample and move to the next distance. Continue to set new samples and increase the drop distance until the film fractures. Continue the procedure until 5 fractures are observed. Calculate the amount of work energy, i.e. the fracture strength using the following formula:

$W = m \times g \times h$, where

W = amount of work energy in ergs,

m = mass of probe (59.53 g) (The probe is removable and can be replaced with one of different mass or impact surface area).

g = gravitational constant (980.665 cm/sec²),

h = average distance probe travels to impact (cm).

The dried hairspray compositions of the present invention preferably have an impact strength of greater than about 7000 ergs, more preferably greater than about 20,000 ergs, and even more preferably greater than about 50,000 ergs.

Hair Spray Removeability

The adhesive copolymers herein have improved removeability when used in the preferred hairspray embodiments of the present invention. In this context, improved removeability means that the adhesive copolymers are more easily removed from the hair or other applied surface during shampooing.

For purposes of defining the preferred hair spray compositions of the present invention, removeability is determined indirectly by evaluating hair stiffness and the appearance of observable white flakes after treating the hair in accordance with the removeability methodology described hereinafter. It has been found that the removeability of a hair spray formulation after shampooing correlates with the resulting stiffness/softness of the hair and the appearance/nonappearance of white flakes on the hair after a series of shampooing cycles. The hair spray compositions of the present invention have high removeability e.g., reduced stiffness and reduced white flaking. The term "removeability" as used herein therefore refers to hair

The hair switches are treated with either an aerosol or non-aerosol hair spray embodiment of the present invention in accordance with the following steps. The hair stiffness reference and the flaking reference are also prepared in accordance with the following steps, except that each is treated with the corresponding hair spray formulations as described hereinafter in Tables 2 and 3.

- 1) Vertically suspend a clean hair switch (10 inch European virgin brown hair, 20 gram) from its bound end and comb (black rubber comb, 5 inches by 1 inch, 1/2 fine tooth) through the switch to remove any tangles.
- 2) If necessary, use a static gun to eliminate any static build-up on the switch.
- 3) For non-aerosol products, spray the switch from a distance of 4 inches while applying ten pumps of the product to the switch and while moving the atomized spray pattern in a fluid up-and-down motion to cover the entire switch, or for aerosol products, spray each switch from a distance of 6 inches while applying the aerosol stream to the switch for a period of 3 seconds and while moving the aerosol stream in a fluid up-and-down motion to cover the entire switch.
- 4) Repeat step 3 on the opposite side of the switch.
- 5) After spraying the opposite side of the switch, hang the treated switch from its bound end to allow it to dry for one hour at ambient temperature, pressure and humidity.
- 6) Comb the dried switch using a black rubber comb (5 inches x 1 inch, 1/2 inch fine tooth) by combing away from the bound end of the switch but by initially starting toward the unbound end taking smaller strokes and then gradually taking larger strokes until the comb passes through the entire unbound length of the treated switch.
- 7) Repeat steps 1 through 6.
- 8) Wet the treated hair switch with water (+15-20 grain hardness, 38°C, 1 gal/min. water pressure).
- 9) Apply 1 ml of shampoo (Table 1: methodology shampoo) along the length of the front of the wet hair switch and apply another 1 ml of the shampoo along the length of the reverse side of the wet hair switch.
- 10) Gently milk the switch from top to bottom (hand over hand between thumb and fingers) for 15 seconds at 1 stroke per second.
- 11) Rinse the hair switch with water (38°C, +15-20 grain hardness, 1 gal/min. water pressure) for 15 seconds. Gently squeeze the hair between the first and

Table 2: High Flaking Control

Raw Materials	Percent Composition As Added	Percent Composition Chemical Content
Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer (National Starch lot AF-6713)	4.50	4.50
Water - USP Purified	15.50	15.50
Ethanol (SDA 40)	80.00	80.00

Table 3: High Stiffness Control

Raw Materials	Percent Composition As Added	Percent Composition Chemical Content
Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer (National Starch lot AF-6713)	6.00	6.00
Aminomethylpropanol, 95%	1.04	0.99
Water - USP Purified	15.50	15.50
Diisobutyl Adipate	0.20	0.20
Ethanol (SDA 40)	80.00	80.00

Each of the formulations described in Tables 1-3 are prepared by conventional formulation and mixing techniques.

Optional Ingredients

The hairspray compositions of the present invention may further comprise one or more optional ingredients known or otherwise effective for use in hairsprays and other hair styling compositions. These optional ingredients may be used to improve or otherwise modify aesthetics, performance or stability of the hairspray compositions. Concentrations of such optional ingredients will vary with the type of material added and its intended performance, but will typically and collectively range from about 0.005% to about 50%, more typically from about 0.05% to about 30% by weight of the composition.

Plasticizers for the silicone-containing adhesive block copolymer are especially useful in the hairspray herein. Suitable plasticizers include any known or otherwise effective plasticizer suitable for use in hair care or other personal care compositions, nonlimiting examples of which include glycerin, diisobutyl adipate, butyl stearate, propylene glycol, tri-C₂-C₈ alkyl citrates, including triethyl citrate

composition in a form such that they can exist in the composition as free ions, i.e., in dissociated form. It is not necessary that all of the ions added exist in the composition as free ions, but must be at least partially soluble or dissociated in the hairspray composition. The ionic strength modifiers can be incorporated into the hairspray compositions, for example, by addition of soluble salts, or by addition of mixtures of acids and bases, or by a combination thereof. When such an optional ionic strength modifier system is used, it is a necessary that both anions and cations of the optional ionic strength modifier system be included in the hairspray composition.

Nonlimiting examples of suitable optional cations for use in the compositions are alkali metals, such as lithium, sodium, and potassium, and alkaline-earth metals, such as magnesium, calcium, and strontium. Preferred of the divalent cations is magnesium. Preferred monovalent metal ions are lithium, sodium, and potassium, more preferably sodium and potassium. Suitable means of addition to the compositions hereof include, for example, addition as bases, e.g., hydroxides, sodium hydroxide and potassium hydroxide, and such as salts that are soluble in the liquid carrier, e.g. salts of monomeric anions such as those described below. Other nonlimiting examples of suitable cations include organic ions, such as quaternary ammonium ions and cationic amines, such as ammonium mono-, di-, and triethanolamines, triethylamine, morpholine, aminomethylpropanol (AMP), aminoethylpropanediol, etc. Ammonium and the amines are preferably provided in the forms of salts, such as hydrochloride salts.

Monomeric anions that can be used include halogen ions, such as chloride, fluoride, bromide, and iodide, particularly chloride, sulfate, ethyl sulfate, methyl sulfate, cyclohexyl sulfamate, thiosulfate, toluene sulfonate, xylene sulfonate, citrate, nitrate, bicarbonate, adipate, succinate, saccharinate, benzoate, lactate, borate, isethionate, tartrate, and other monomeric anions that can exist in dissociated form in the hair styling composition. The anions can be added to the compositions hereof, for example, in the form of acids or salts which are at least partially soluble in the liquid vehicle, e.g., sodium or potassium salts of acetate, citrate, nitrate, chloride, sulfate, etc. Preferably, such salts are entirely soluble in the vehicle.

Other optional ingredients include surfactants (which may be anionic, cationic, amphoteric, or zwitterionic and which include fluorinated surfactants and silicone copolyols), propellants, hair conditioning agents (e.g., silicone fluids, fatty esters, fatty alcohols, long chain hydrocarbons, cationic surfactants, etc.); emollients; lubricants and penetrants such as various lanolin compounds; protein hydrolysates and other protein derivatives; ethylene adducts and polyoxyethylene

Patent 4,077,441, March 7, 1978, Olofsson; U.S. Patent 4,850,577, July 25, 1989, TerStegé; and U.S. Serial No. 07/839,648, Gosselin et al., filed February 21, 1992, which descriptions are incorporated herein by reference. The hairspray compositions of the present invention may also be dispensed in any known or otherwise effective means for delivery to the hair, including any known or otherwise effective atomizing means such as a nonaerosol pump spray device.

Method of Making

The hairspray compositions of the present invention can be made using conventional formulation and mixing techniques. For example, the silicone-containing adhesive block copolymer and the alcohol solvent are combined and mixed together to form a homogeneous solution or dispersion. Other ingredients are then added to the homogenous solution or dispersion and mixed to yield the hairspray composition of the present invention. If the silicone-containing adhesive block copolymer is neutralized, the neutralizer is preferably added prior to addition of other ingredients. The hairspray composition is then packaged in a conventional or otherwise suitable mechanical pump spray device, or alternatively, in the case of aerosol hairspray compositions, the hairspray composition is packaged in a conventional or otherwise suitable aerosol canisters along with an appropriate propellant system.

Method of Use

The hairspray compositions of the present invention may be used in a conventional manner to provide the desired hair styling benefits. Such methods generally involve application of an effective amount of the composition to dry hair which has been arranged or positioned in the desired style. In this context, the term "effective amount" means an amount sufficient to provide the hair hold and style benefits desired, typically an amount ranging from about 0.5 grams to about 30 grams of the composition, depending upon the selected hairspray composition and formulation, dispenser type, length of hair, type of hair style, and so forth. The composition is applied to the hair by spraying or atomizing the composition using a mechanical pump spray device, a pressurized aerosol container, or other appropriate delivery means. The composition is then dried or allowed to dry on the applied surface.

The following Experiments and Examples further illustrate embodiments within the scope of the present invention. They are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as

temperature of the block B of the resulting polymer is between about -20°C and 60°C.

Polymer 1.2 [Poly(dimethyl siloxane)-block-poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)]_n

Place 80 parts of t-butyl acrylate, 56 parts n-butyl acrylate, 12 parts acrylic acid, 10 parts methacrylic acid, 400 parts acetone (as a solvent), and 50 parts isopropanol (as a chain transfer agent) in a roundbottom flask. Separately, dissolve 20 parts VPS-1001 (poly(dimethyl siloxane) initiator) macroazoinitiator (commercially available from Wako Chemical USA, INC., Richmond, VA) into 400 parts ethyl acetate, add to this solution 12 parts acrylic acid and 10 parts methacrylic acid, and add the solution to an addition funnel. Purge the reaction vessel with argon for approximately one hour. Following the purge, maintain a constant positive pressure on the closed reaction system with argon. Heat the reaction mixture to 58°C. Add the VPS-1001 solution to the reaction flask in a dropwise fashion over the course of one hour. Maintain heating and stirring for 20 hours. Terminate the reaction by opening the reactor to the atmosphere and cooling to room temperature.

The block copolymer is precipitated from the solution by adding one part of the polymer solution to 15 parts water. The resultant polymer is redissolved in acetone and is precipitated again from 15 parts water. The resultant block copolymer is then placed in a vacuum oven for heated drying. Following the drying, the polymer is ground and extracted for 20 hours with hexane using a soxhlet extractor. The polymer is then vacuum dried with heat in an oven. The glass transition temperature of the block B of the resulting polymer is between about -20°C and 60°C.

Example 2

The following examples represent specific aerosol hairspray embodiments of the present invention.

Component (wt%)	<u>Example Number</u>					
	2.1	2.2	2.3	2.4	2.5	2.6
Copolymer 1.1	5.00	4.00	3.50	---	---	---
Copolymer 1.2	---	---	---	5.00	4.00	3.50
Isododecane ¹	0.50	---	---	0.50	---	---
Triethyl citrate ²	--	--	0.21	--	--	0.21
Diisobutyl adipate	0.70	0.45	--	0.70	0.45	--

Component (wt%)	<u>Example Number.</u>							
	3.1	3.2	3.3	3.4	3.5	3.6	3.7	3.8
Copolymer 1.1	4.00	5.00	6.00	4.00	---	---	---	---
Copolymer 1.2	---	---	---	---	3.00	3.50	2.50	4.00
Isododecane ¹	1.00	---	---	---	---	1.0	2.0	---
Diisobutyl adipate	0.40	---	0.90	0.55	---	---	---	0.40
Sodium hydroxide ²	0.96	1.20	1.44	---	---	1.20	---	1.35
Potassium hydroxide ³	--	--	--	1.21	1.00	--	0.70	--
Perfume	0.10	0.10	0.10	0.10	0.10	0.15	0.10	0.15
Water	QS10	QS10	QS10	QS10	QS10	QS10	QS10	QS10
	0	0	0	0	0	0	0	0
Sodium Benzoate	--	--	--	--	0.10	0.10	--	0.10
Ethanol ⁴	76.54	71.95	81.56	71.25	79.40	69.26	78.00	55.00

¹ PERMETHYL 99A, from Presperse, Inc., South Plainfield, NJ, USA.

² Sodium hydroxide is 30% active.

³ Potassium hydroxide is 45% active.

⁴ SDA 40 (100% ethanol).

The exemplified hairspray compositions 3.1-3.8 are prepared as described above, by first mixing the silicone-containing adhesive block copolymer (polymer 1.1 or 1.2) with ethanol, neutralizing the polymer with sodium or potassium hydroxide, then adding sequentially (as applicable) with mixing, isododecane, plasticizer, perfume, and water. If sodium benzoate is used, it is added after water addition. Most preferably a premix of water and sodium benzoate is made and then added after the main water addition.

Each of the exemplified hairspray compositions in Examples 2 and 3 are specific embodiment of the hairspray compositions of the present invention, and provide improved hair styling performance when applied to dry, styled or positioned hair, and in particular provide improved maintenance or hold when applied to dry hair and causes minimal or no drooping of the hair during or immediately after application.

Each of the exemplified hair spray compositions in Examples 2 and 3 also provide improved removability from hair, and when evaluated by the removability methodology described herein, provide a hair stiffness value of less than 2.0 and a hair flaking value of less than 2.0.

2. The hairspray composition of any one of the preceding claims wherein the alcohol solvent is selected from the group consisting of ethanol, n-propanol, isopropanol, and mixtures thereof, and wherein the adhesive block copolymer is solubilized in the hairspray composition.
3. The composition of either of any one of the preceding claims wherein the silicone macroinitiator is a silicone macroazoinitiator where Y is an azo group.
4. The composition of any one of the preceding claims wherein the block copolymers comprise from about 60% to about 95% by weight of the copolymerized ethylenically unsaturated monomers, and from about 5% to about 40% by weight of the copolymerized silicone macroinitiators.
5. The composition of any one of the preceding claims wherein m has a value of from about 14 to about 700, n has a value of from about 1 to about 10, and the silicone macroazoinitiator has a number average molecular weight of from about 5,000 grams/mole to about 100,000 grams/mole.
6. The composition of any one of the preceding claims wherein the composition, when dried, has a cohesive strength of greater than about 0.5 kgf/mm^2 , a total energy absorption per unit volume of greater than about 0.55 kgfmm/mm^3 and an impact strength of greater than about 7000 ergs.
7. The composition of any one of the preceding claims wherein the composition, when dried, has a cohesive strength of greater than about 0.7 kgf/mm^2 , a total energy absorption of greater than about 1.10 kgfmm/mm^3 , and an impact strength of greater than about 50,000 ergs.

1/1

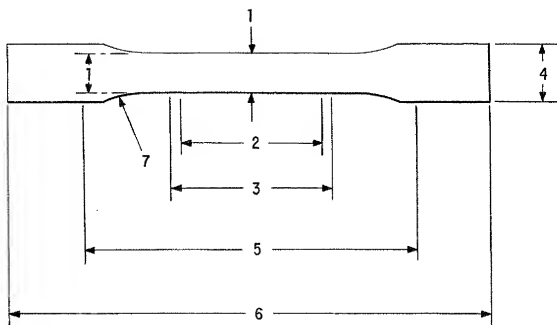


FIG. 1

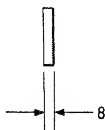


FIG. 2

INTERNATIONAL SEARCH REPORT

Information on patent family members

national Application No

PCT/IB 98/00754

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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